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Dziennik Ustaw.

FOLISH DECREE ON AREAS VITAL TO NATIONAL DEFENSE

Item 341 - Decree of 6 September 1951

In accordance with Article 4 of the Constitutional Law, dated 19 February 1947, on the organization and competence of the supreme authorities of the Republic of Poland, and in accordance with the law, dated 26 May 1951, on author-Ustaw Rzeczypospolitej Polskiej, No 30, Item 235), the Council of Ministers decrees and the Council of State confirms the following:

Article 1. Paragraph 1. The Council of Ministers may, on the recommendation of the Minister of National Defense, declare certain areas as particularly important for national defense, may limit the rights of ownership, possession, use, and benefit from real estate, may restrict visits or residence therein, and may restrict specific activities such as surveying, topographic study, photography, peddling, taxi service, or other enterpreneurial services, etc.

Paragraph 2. The area in every case will be determined in detail by the Council of Ministers, which will also specify the restrictions which are to be enforced in this region, and whether general and specific dwelling regulations apply. The council is to issue regulations concerning construction or alteration of buildings in fortified and reinforced areas.

Article 2. Paragraph 1. Whoever suffers actual loss because of the laws on real estate or any laws affecting real estate because of limitations mentioned in Article 1 or because of being forbidden permission to discharge these rights is entitled to indemnity from the state.

Paragraph 2. The right to receive indemnity does not apply to those who at the time the restrictions were put in force in accordance with the present decree had already been subject to these conditions because of previously existing regulations limiting rights pertaining to real estate.

Paragraph 3. The right to indemnity expires after the lapse of 3 years from the moment that the restrictions are effective or from the time of the legalization of the limitation.

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Paragraph 4. The Council of Ministers will issue a directive on the competence of authorities, the principles of determining and paying indemnity, and procedure.

Article 3. The Council of Ministers will define the principles of cooperation of interested state authorities in executing this decree and will legalize the relations of these authorities to the population in areas acknowledged as particularly important for national defense.

Article 4. Existing restrictions on the basis of previous regulations on fortified and reinforced areas remain in force until regulations mentioned in Article 1 are issued for these areas.

Article 5. Up to the time regulations mentioned in Article 2, Paragraph 4, are in force, regulations in effect heretofore will apply to claims for indemnities on the basis of restrictions mentioned in Article 4.

Article 6. The Council of Ministers may, on the recommendation of the Minister of National Defense, modify the limitations on rights in fortified and reinforced areas (Article 4) and restrictions introduced on the basis of Article 1.

Article 7. The Council of Ministers will specify the manner in which the population in an area considered particularly important for national defense is to be informed on limitations which are to be introduced or modified and on the legal relationship between the state authorities and the population in these areas.

Article 8. Whoever infringes upon regulations issued in accordance with this decree or fails to comply with the orders of the authorities ordered to enforce this decree is liable to 3-month imprisonment or a 4,500-zloty fine, or both.

Paragraph 2. The sentence is imposed according to criminal administrative procedure.

Article 9. This decree supersedes the following:

Paragraph 1. The directive of the President of the Republic, dated 10 July 1927, on designating certain areas and localities as fortified or reinforced areas (Dziennik Ustaw Rzeczypospolitej Polskiej, No 55, Item 483),

Paragraph 2. The law, dated 28 January 1932, on the legal relations in fortified and reinforced areas (Dziennik Ustaw Rzeczypospolitej Polskiej, No 19, Item 124), and

Paragraph β . All legal regulations passed by former occupation authorities pertaining to fortresses and fortifications.

Article 10. The Chairman of the Council Ministers, the Minister of National Defense, and other interested ministers are committed to execute this decree.

Article 11. The decree of $\ensuremath{\mathsf{6}}$ September 1951 becomes effective on the day of its publication.

B. Bierut, President of the Republic J. Cyrankiewicz, Chairman of the Council of Ministers K. Rokossovskiy, Minister of National Defense

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PROBLEM OF THE ELECTROCHEMICAL PROPERTIES OF MICKEL

Yu. V. Baymakov, L. M. Yevlannikov Leningrad Polytechnic Institute imeni M. I. Kalinin Submitted 11 April 1950

Figures referred to are appended. 7

The diversity of the electrochemical properties of nickel has taken the attention of many electrochemists. Independent of the character of solution and gaseous medium, the values of its potential vary from -0.4 to+0.30 v. Haring and Bousche /1/ produced data on projects connected with numerous attempts at extermining the normal potential of nickei. However, no one has raised a question concerning the relation of potential to the nature of the metal. This problem was placed before the authors during a study of the potentials of very pure nickel.

Rlectrolytic nickel obtained from solutions thoroughly purified of copper, cobalt, and iron was used in the investigation. The metal obtained did not produce a qualitative reaction on copper, iron (ether extraction after the addition of ammonium rhodanide), or cobalt (Fogel's reaction). The metal contained 0.0025% sulfur.

The precipitate of electrolytic nickel consisted of fibrous crystals situated perpendicular to the plane of the electrode. Average crystal length was 0.02 mm; cross-section size was 0.0015 mm (Figure 1)

During heating of the electrolytic nickel, starting at 700° C, recrystallization occurs and, at 1,200° C, ends with the formation of a nolvhedral structure (Figure 2)

metal recrystallizes in grains of from 0.04 to 0.3 mm cross section, and twinned formations are found, attesting to the presence in the original metal of internal stresses, removed by heating.

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Heating of the nickel samples was conducted in a vacuum furnace. The furnace was equipped with a device which allowed determination of the rate of hydrogen elimination relative to increase in the heating temperature /27. At a temperature of 450° C there was observed the first maximum of the hydrogen elimination rate, with the second occurring at $1,100^{\circ}$ C.

The total amount of hydrogen separated was equal to 0.018 mole per mole of nickel (1.8 mol %), with the quantity of hydrogen separated at 450° equal to 0.4 mol %.

Thus, electrolytic nickel might be said to contain hydrogen of two categories, with separation of the second portion of hydrogen beginning at a temperature determined to be of the order of 700° , and reaching a maximum at $1,100^{\circ}$. No matter how long the samples were burned, secondary elimination of hydrogen was not observed at a lower temperature (say 600°).

Nickel heated in vacuo may be reimpregnated with hydrogen by prolonged cathode polarization of the metal in a sulfuric acid solution. The heating of nickel which has been reimpregnated with hydrogen is accompanied by separation of the hydrogen; but on a graph of the separation rate, a maximum is observed only at 450-500°. The second maximum is not observed.

From this point on we shall designate the original precipitate of the metal as "electrolytic," and that heat treated in vacuo as "metallurgical." In addition, we shall designate the hydrogen released at 400-500° as hydrogen No 1, and that released at 700 to 1,200° as No 2.

M. S. Beletskiy took Debye roentgenograms of samples of electrolytic and metallurgical nickel. The electrolytic nickel has a face-centered cubic lattice with spaces, a, equal to 3.50 A. The roentgenogram of electrolytic nickel does not have clear lines; they are blurred. The roentgenogram of metallurgical nickel shows an equal to 3.490 A, and the lines are clear.

The roentgenogram of metallurgical nickel reimpregnated with hydrogen has clear lines and, by its indexes, corresponds fully with metallurgical nickel (a = 3.490 A). There are in the literature indications that nickel may absorb from 4 to 3,400 volumes of hydrogen. This diversity of data is probably attributable to different conditions of impregnating the nickel with hydrogen, and to the variety of methods used in determining its content in the metal. It is further indicated that by reduction of an ether solution of nickel chloride with magnesium phenylbromide, nickel hydrides of composition NiH, and NiH₂ are obtained 37. It can be seen from the data which we have obtained that electrolytic nickel contains hydrogen No 1 weakly bonded with the crystal lattice of the metal and having no effect on the lattice parameters, and hydrogen No 2, strongly bonded with the metal lattice and influencing its parameters. It is difficult to explain the presence of a hydride. It is possible to assume that part of the hydrogen occurs in the form of an atomic solution; the other part enters into the composition of the crystal lattice in the form of a chemical compound or solid solution of penetration. It is most probable that the generation of a stable solid solution of hydrogen No 2 in the nickel with an altered crystal lattice is possible only in the case of coincident release of nickel and hydrogen at the cathode. Cathodic impregnation of metallurgical nickel with hydrogen produces only an atomic solution of hydrogen No l in nickel.

Electrochemical Properties of Electrolytic Nickel

Measurements were taken of the potentials of nickel in the static state, and also in the process of anodic polarization of the metal. The measurements of static potentials were conducted at a constant temperature in normal solutions of chemically pure nickel sulfate.

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Measurements of the potentials during anodic polarization were conducted by the method of direct reading of the potential on the scale of a galvanometer with very high resistance. A schematic diagram of the apparatus used is shown in Figure 3. The ratio of the current in the circuit feeding the electrolysis cell through the voltage divider to the current used by the circuit, which includes the calomel electrode and galvanometer, was quite large. The current applied on the electrode varied from 1·10-5 to 2,000·10-5 A/sq cm. The current in the measuring circuit varied from 4·10-9 to 200·10-9 A. The galvanometer was graduated in emf values by the compensation method; however, the measurement of potentials by this method was impossible in view of their rapid change. It was this fact which accounted for the use of the high-resistance galvanometer.

Potentials of Electrolytic Nickel in a Hydrogen Medium

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Measurements were conducted in a solution of chemically pure nickel sulfate (no chlorine ion content) with various hydrogen ion concentrations, at constant temperature. Hydrogen gas, containing no sulfur and thoroughly purified of oxygen, was passed continuously through the vessel.

The potential was stabilized over a period of several tens of minutes. The results are shown in Figure 4. It is seen that the potential of electrolytic nickel depends on the pH value; and with a pH value between 2 and 6 this dependence is expressed by the equation:

$$\varepsilon_{1} = -0.012 + 0.058 \text{ lg } / \overline{\mathbb{H}}^{+} / 7.$$
 (1)

With pH values from 0 to 2 the potential values do not conform to this dependence. It is seen on the graph that the values for the nickel potentials coincide with the potential values of the hydrogen electrode in the pH range from 2 to 6. Thus, the nickel, in that pH interval, appears as the hydrogen electrode. It ceases this behavior at pH values below 2. On the same graph, there appear the potentials for samples of electrolytic nickel which were heated in a hydrogen medium to a temperature of 450 and 650° C. It is seen here that the values obtained are more electropositive, tending away from a linear dependence. The observations made allow examination of the potential formed on the nickel as a compromise caused by a complex of reactions:

$$\mathbb{H} \to \mathbb{H}^+ + \Theta \longrightarrow \Phi_1 \tag{2}$$

$$Ni \rightarrow Ni^{++} + 2 \ominus \cdots \Phi_2$$
 (3)

$$\mathbf{H}^{+} + \Theta \rightarrow \mathbf{H} \dots \Phi_{3} \tag{4}$$

$$Ni^{++}+2\Theta \rightarrow Ni \dots \Phi_4.$$
 (5)

The quantities from Φ_1 to Φ_4 correspond to the rates of the reactions.

The rates of the exchange reactions may be expressed as exponential dependences on the energy-of-activation values 24.7.

$$\Phi_{1} = k_{1} \exp \frac{\alpha_{1} \Delta \epsilon_{1} F}{ET},$$

$$\Phi_{2} = k_{2} \exp \frac{\beta_{2} \Delta \epsilon_{2} 2F}{RT},$$

$$\Phi_{3} = k_{3} / \overline{H}^{+} / \exp \frac{-\alpha_{3} \Delta \epsilon_{3} F}{RT},$$

$$\Phi_{4} = k_{4} / \overline{M}^{1+} / \exp \frac{-\beta_{4} \Delta \epsilon_{4} 2F}{RT}.$$
(6)

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It is apparent from the data presented that for electrolytic nickel in the pH interval from 2 to 6, the quantities Φ_2 to Φ_k are practically equal to zero. Therefore, the compromise potential on nickel in a hydrogen medium is determined by the equivalence:

$$\Phi_1 = \Phi_3. \tag{7}$$

Under conditions when only the hydrogen ion participates in the exchange reaction, the value of the compromise potential in the equilibrium state may be expressed as $\varepsilon_k = \Delta \varepsilon_1 = \Delta \varepsilon_3$, using the values from (6) in (7). Using logarithms, (7) is then solved from e_k ; taking into consideration that $\alpha_1 + \alpha_3 = 1$, we obtain

$$\varepsilon_{\mathbf{k}} = \frac{\mathbf{RT}}{\mathbf{F}} \ln \frac{\mathbf{k}_3}{\mathbf{k}_1^3} + 0.058 \lg \sqrt{\mathbf{R} + 7}, \tag{8}$$

which coincides with expression (1), derived from the experimental data. In the given case, $\varepsilon_{\rm K}$ is equal to the equilibrium hydrogen potential on nickel.

In the case when only nickel ions participate in the exchange reaction, the expression for the potential is derived from the condition, $\Phi_2 = \Phi_{\downarrow}$, and assumes the value of the equilibrium nickel electrode:

$$\varepsilon_{\mathbf{k}} = \frac{\mathbf{R}\mathbf{T}}{2\mathbf{F}} \ln \frac{\mathbf{k}_{\mathbf{k}}}{\mathbf{k}_{2}} + \frac{\mathbf{R}\mathbf{T}}{2\mathbf{F}} \ln \sqrt{\mathbf{N}} \mathbf{i}^{++} \overline{J}. \tag{9}$$

With pH < 2 in the hydrogen medium, and for heat-treated nickel, over a wider pH range, deviations from the relationship in (8) are observed. Bot only reactions (1) and (3), but also (2) and (4) participate in the exchange; however, $\Phi_1 \neq \Phi_3$; $\Phi_2 \neq \Phi_b$, i.e., nickel ions may transfer into the solution, while hydrogen is partially released from the solution. In this case, the value for the compromise potential must lie between the extremes expressed by equations (8) and (9). The value of the compromise potential is derived from the condition:

$$\Phi_1 + \Phi_2 = \Phi_3 + \Phi_4. \tag{10}$$

An expression for the compromise potential ϵ_k may be obtained in the following manner: substitute in expression (10) the values of Φ_1, \dots, Φ_k from (6), broken down into series. Substitute the quantity $\Delta \epsilon_k = \epsilon_k - \epsilon_p$, where ϵ_p is the equilibrium potential for the given electrochemical reaction.

These values are substituted in the expression obtained which is solved for $\boldsymbol{\epsilon}_k.$

Expressions for ϵ_p^H and ϵ_p^{N1} are introduced into the resulting expression. These expressions ere:

$$\begin{cases}
\varepsilon_{p}^{Ni} = \varepsilon_{0}^{Ni} + \frac{RT}{2} \ln \sqrt{N}i^{++}, \\
\varepsilon_{p}^{H} = \varepsilon_{0}^{H} + \frac{RT}{F} \ln \sqrt{B}i^{+},
\end{cases}$$
(11)

where $\epsilon_0^H=0$, since it is the normal potential of hydrogen on nickel.

The final expression is:

$$\varepsilon_{k} = A\varepsilon_{0}^{H} + B\varepsilon_{0}^{N1} + A \stackrel{RT}{F} \ln \left(\overline{H} + \overline{f} + B \stackrel{RT}{2F} \ln \left(\overline{N} \right)^{+} \right) + (A + B) \stackrel{RT}{F} (k_{3} \overline{H} + \overline{f} + \frac{1}{2}k_{4} \overline{N} \right)^{+}.$$
(12)

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The constants A and B are more complex expressions in which the constants and coefficients, respectively, from the expressions (6) are incorporated. In the case of the absence of exchange reactions by the nickel ions, the values of Φ_2 and Φ_4 are equal to zero. Expression (12) is converted into an equation analogous with expression (8).

Expression (12) is a second-order equation. As the values for Φ_2 and Φ_4 increase, the items pertaining to nickel increase, while the values of ϵ_k for different pH depart more and more from the values obtained from expressions (8) and (1). This is quite apparent from the data shown in Figure 4.

Potential of Electrolytic Nickel in Presence of Atmospheric Oxygen

An electrode of electrolytic nickel was immersed in a solution of chemically pure nickel sulfate. The potential was measured periodically. The results are shown on the graph (Figure 5). The time is plotted on the abscissation in logarithmic scale.

The potential remains at 0.02-0.03 v for a period of 1,000 minutes, then rises to 0.18-0.19 v; and this period of stabilization continues for from 200 to 670 hr. Following this, there is another rise in potential, with subsequent stabilization up to 0.26-0.28 v.

In the given case, the picture of the electrochemical reactions which determine the value of the compromise potential is complicated by the fact that oxygen was dissolved in the electrolyte.

It is possible to assume the existence of electrochemical reactions which determine the exchange, as follows:

Stabilization of the potential is possible under the condition:

$$\Phi_1 + \Phi_2 = \Phi_3 + \Phi_4 + \Phi_5$$
.

In the first period of formation of the electrode, the high rate of formation of hydrogen ions Φ_1 compensates the quantity of hydroxyl ions formed. The demand in hydrogen ions for reactions involving the utilization of oxygen and hydrogen peroxide is undoubtedly great, and the value of Φ_5 , expressed in coulombs, is indisputably considerable. This initial period of the "neutralization" of the reaction products from the reduction of the oxygen by the hydrogen ions formed most probably is characterized by a compromise potential fundamentally determined by the equivalence:

$$\Phi_1 + \Phi_2 = \Phi_5,$$

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Reactions corresponding to the exchange of Φ_2 and Φ_4 take place to the extent dictated by a monomolecular layer of oxygen on the nickel. The reaction of Φ_3 is suppressed by the Φ_5 reaction complex.

By measure of the expenditure of electrochemically active hydrogen in the electrolytic nickel, compensation of the reaction products with respect to Φ_5 is disturbed. The excess OH causes a film of Ni(OH)₂ to form, hindering the course of the reactions Φ_1 and Φ_2 .

The absolute values of the sums $\Phi_1+\Phi_2=\Phi_3+\Phi_1+\Phi_5$ drop. The exchange is accomplished at the expense of Φ_1 and Φ_2 , on the one side, and Φ_5 on the other. There is established a compromise potential close to the equilibrium potential of the oxygen-reduction reaction.

Finally, terminal passivity of the metal sets in with a considerable reduction of exchange current and the establishment of a potential close to the reaction complex (5).

Extremely interesting with respect to the characteristic of the nickel potential is its dependence on pH value. The experiment proceeded as follows: A nickel electrode was immersed in a solution of ${\rm NiSO_h}$ with pH equal to 6. The stabilizing potential was measured. The solution was then poured into a vessel and replaced by a sulfate solution of pH value 4, measurement was made of stabilizing potential, etc. It was established that at pH values from 6 to 2.3, the stabilizing potential is +0.20 to +0.22 v. At a pH of 2.31, there occurs a sharp drop in stabilizing potential, to +0.04.

Figure 6 shows values for the pH range from 3.23 to 2.00. This interesting phenomenon may be explained as follows: In the pH interval between 6 and 2.41, the concentration of hydrogen ions is inadequate to compensate the formation of hydroxyl ions in the second and third stage of potential stabilization (Figure 5), and prevent the formation of stable passive films on the nickel. At a pH value of 2.31, and below, the amount of hydrogen ions increases to a point where the quantity of OH is compensated by an excess of H+, and passivity of the nickel is determined by a molecular layer of oxygen. The potential is determined as a compromise potential of the reactions Ni \rightleftharpoons Ni+++ \rightleftharpoons and

Anodic Polarization of Electrolytic Nickel

An electrode of electrolytic nickel was subjected to anodic polarization with continuous measurement of the potential at the electrode. Measurements were made with the use of the circuit shown in Figure 3.

The results are shown in Figure 7. With a pH in the solution of from 6 to 2, passivity of the metal is observed at slight current values. Anodic dissolving of the nickel is encountered only at a pH of 1.16, but with a current of about 0.05 mA/sq cm, it is passivated and the potential at the anode increases to values corresponding to hydroxyl-ion discharge.

The behavior of electrolytic nickel shows up particularly well from an analysis of the curves of variation in current and potential recorded on a time scale (Figure 8). The potential value of 0.10 v increases to a value of 0.30 v. At the same time, the current increases to a value of 13:10-6 A. A drop in current value to 2-3:10-6 A then sets in, during which time the potential value continues to increase. At a potential value corresponding to mass hydroxyl discharge, the curve showing current values starts to climb.

Consequently, the greatest slowing down in the reaction of nickel-ion formation is observed during the anodic polarization of electrolytic nickel.

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Electrochemical Properties of Metallurgical Nickel; Measurement of Potentials in a Hydrogen-Saturated Medium

The potentials of metallurgical nickel were measured in a lN solution of chemically pure nickel sulfate. On the basis of the data obtained, a curve was plotted for the potential dependence on pH (Figure 9). In the same figure, there are presented for comparison the potential values for electrolytic nickel measured under the same conditions. It is evident from a comparison of the data that the relationship found here does not correspond to equation (8), and is one of the solutions of equation (12) for a compromise potential, i.e., in the given case, there are real values for the rates of Φ_2 and Φ_4 at all pH values.

Measurement of Potentials of Metallurgical Nickel in Solutions Saturated With Air

The potential of metallurgical nickel in a 1N solution of nickel sulfate was established for a period of several hours within the limits of the values 0.18-0.28 v, dependent on pH (Figure 10).

It should be noted that in the transition of pH values from 2.5 to 2.0, a sharp change in potential was not observed. Such a change was observed, however, in the case of electrolytic nickel. This is most probably attributable to the fact that in the combination of the electrochemical reactions (2), (3), (4), (5), reaction (2) is, practically, absent, and the value of Φ_2 is considerably higher, since reaction (3) is the basic compensator of charges, which compensator is required by the system of reactions (3).

Anodic Polarization of Metallurgical Nickel

The experiments were conducted under conditions analogous to those prevailing in the study of electrolytic nickel. The data are shown in Figure 11. With a pH of 6.2, passivity sets in at 2.0 mA/sq cm. With lower pH values, passivity sets in at 15-80 mA/sq cm. Consequently, metallurgical nickel is considerably more active then electrolytic nickel. It is interesting to note that this unexpected passivity sets in, in all cases, at an anode potential close to 0.30 v. such a potential value may be obtained in the case of the polarization of electrolytic nickel at a current of 10-15 10^{-6} A/sq cm, and in the case of metallurgical nickel, at 2,500-80,000 10^{-6} A/sq cm.

Anodic Polarization of Metallurgical Nickel Reimpregnated With Hydrogen

The data are presented in Figure 12 and show that with reimpregnation by hydrogen, the activity of metallurgical nickel is preserved.

Nature of Hydrogen in Nickel and Its Effect on Electrochemical Properties

A comparison of the amount of hydrogen in the metal--the hydrogen being contained in two forms--with roentgenographic data leads to the conclusion that the hydrogen weakly bonded with the metal and separable at a low temperature is adsorbed hydrogen or an atomic solution of hydrogen in the metal. This form of hydrogen has no effect on the character of the crystal lattice of the metal and no effect on the electrochemical properties of the nickel. Metallurgical nickel retains a high activity regardless of its content of that form of hydrogen.

An equation deduced by A. N. Frumkin connects the exchange-current value with the polarization value:

$$\Delta \varepsilon = -\frac{RT}{nF} \frac{i}{i_{exch}}$$

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When examining the curves for the dependence of potential on current density, which curves evolved during the anodic dissolving of metallurgical nickel (Figures 11 and 12), it is seen that, as the current increases from zero to 15,000·10⁻⁶A, the anode potential is changed by 0.05-0.2 v. During the anodic dissolving of electrolytic nickel, the potential changes by 0.2 v as the current is varied from zero to 15·10⁻⁶ A (Figure 7).

Thus, despite the fact that the potential of metallurgical nickel is displaced from the equilibrium normal--0.23 v, to a value of 0.1 v, due to the presence of a molecular layer of oxygen, we nevertheless establish the presence of high exchange currents because of the reactions (3)-(5).

On the other hand, electrolytic nickel is characterized by very small exchange currents (even at low pH values).

Electrolytic nickel contains the first form of hydrogen; but, in addition, it contains hydrogen in a form which distorts the crystal lattice of the metal and, as is seen from the data presented, changes the electrochemical properties of the nickel, making it more passive. The character of the lattice distortion leads to the assumption that with the introduction of protons into the lattice, a solid solution is formed with collectivization of the valence electrons, but with an increased charge density around the protons. The high passivity of the electrolytic nickel may be explained by the fact that the protons in the crystal lattice set up electric fields on the surface of the crystals, which fields are stronger than those formed by the nickel ions. These fields are conducive to the formation of a denser binary electric layer with oxygen atoms or hydroxyls, which layer obstructs the exchange reactions and increases polarization during the process of nickel-ion formation.

The picture would then appear as follows: In the process of discharge at the cathode, cations of nickel enter into the crystal lattice of the metal co-incidentally with the discharge of hydrogen cations. The hydrogen cations released from the hydrate envelopes are protons with a radius of the order of $1\cdot10^{-13}$ cm. One portion of the protons is adsorbed by the surface of the nickel crystal, is neutralized by electrons, and forms atoms which are partially dissolved in the metal or form molecules. The other portion of the protons enters into the crystal lattice along with nickel ions and forms a solid solution of penetration.

In the practical utilization of nickel, it was noted that metallurgical nickel corrodes noticeably under conditions in which a precipitate of electrolytic nickel shows absolutely no corrosion. This difference of electrochemical properties in metallurgical and electrolytic nickel becomes explicable in the light of the data obtained.

Conclusions

- l. Electrolytic nickel was analyzed for hydrogen. It was shown that part of the hydrogen separates out at $400-500^\circ$, the other part at $700-1,000^\circ$ C.
- It was shown that metallurgical nickel from which the hydrogen had been separated may be reimpregnated with hydrogen by the cathodic polarization method. However, hydrogen introduced into the nickel separates out at 400-500°C.
- 3. Roentgenograms of electrolytic and metallurgical nickel were studied. The roentgenogram of electrolytic nickel shows the presence of a solid solution of variable composition, while that of metallurgical nickel, by the character of the lines, coincides with data derived from roentgenograms of pure nickel.

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4. Data from the study of the electrode potentials show that electrolytic nickel is distinguished by high passivity, while metallurgical nickel is

5. Assumptions are stated regarding the formation of a solution of atomic hydrogen in nickel which does not influence the reduction electrochemical activity in the metal, and regarding the formation of a solid solution of penetration in which hydrogen occurs in the form of protons. This type of solid solution occasions the high degree of passivity.

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Appended figures follow.7

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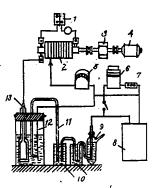


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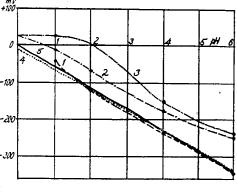
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Figure 3. Apparatus Used for Measurement of Potentials: 1-storage battery; 2-revolving rheochord; 3-rpm reducer; 4-electric motor; 5-galvanometer; 5-multiflex galvanometer; 7-supplementary resistances: 0.5·106, 1.0·106, 2.0·106Ω; 8-five-stage potentiometer; 9-calomel comparison electrode with saturated KCl; 10-intermediate vessels; 11-electrolytic fourtains; 12-test electrode; 13-auxiliary electrode.

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Figure 4. Potentials on Electrochemical Nickel Relative to pH of Electrolyte in a Hydrogen Medium: 1-nickel treated
with H₂ at 20°C; 2-nickel -20°C
3-nickel treated with H₂ at 45°°C;
3-nickel treated with H₂
at 65°C; 4-compromise
potential of N₁ at 20°C,
calculated by formula
(1); 5-equilibrium potential of hydrogen electrode
at 20°C.



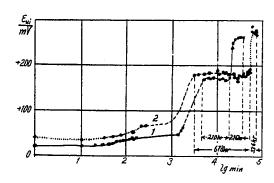


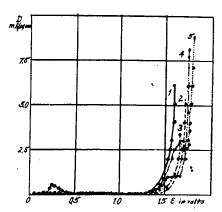
Figure 5. Potentials on Electrolytic Nickel in a Normal Nickel Electrolyte With pH=3 Relative to Time of Testing: 1-pure electrolytic nickel (sample No 1); 2-same (sample No 2).

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Figure 6. Potentials on Electrolytic Nickel Relative to Electrolyte pH and Time of Testing



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Figure 7. Anode Potentials During Polarization of Electrolytic Nickel. 1-pH, 6.28; 2-pH, 3.98; 3-pH, 3.24; 4-pH, 2.18; 5-pH, 1.16.



Figure 8. Effect of the Degree of Polarization of the Electrolytic Nickel on Anode Potential and Current Density.

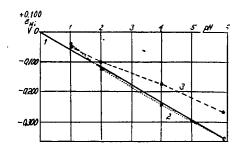


Figure 9. 1-equilibrium potentials of hydrogen electrode at $20^{\circ}\mathrm{C}$; 2-potentials on electrolytic nickel in a hydrogen medium at $20^{\circ}\mathrm{C}$; potentials on metallurgical nickel in a hydrogen medium at $20^{\circ}\mathrm{C}$.

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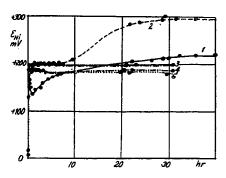


Figure 10. Potentials on Heat-Treated Electrolytic Nickel Relative to Electrolyte pH and Time of Testing: 1-pH, 6.58; 2-pH, 4; 3-pH, 3.2; 4-pH, 2.5; 5-pH, 2.0.

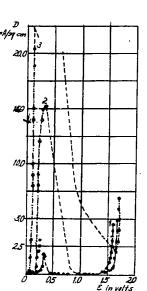
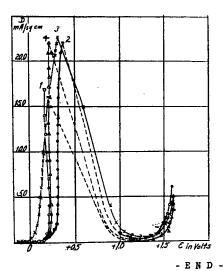


Figure 11. 1-pH, 6.28; 2-pH, 3.24; 3-pH, 1.16.



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Figure 12. 1-metallurgical nickel treated in hydrogen atmosphere at 20°C for 24 hr; 2-nickel treated with hydrogen at cathode in solution of 1N -H₂SO₄ +40g/1 K₂SO₄ for 1,40°O hr; 3-nickel cathode-treated with hydrogen in same electrolyte in hydrogen atmosphere for 60 hr; 4-nickel not treated with hydrogen.

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